

(12) UK Patent Application (19) GB (11) 2 295 101 (13) A

(43) Date of A Publication 22.05.1996

(21) Application No 9422550.5

(22) Date of Filing 09.11.1994

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(51) INT CL⁶
B01D 53/70

(52) UK CL (Edition O)
B1L LAE L102 L306 L604

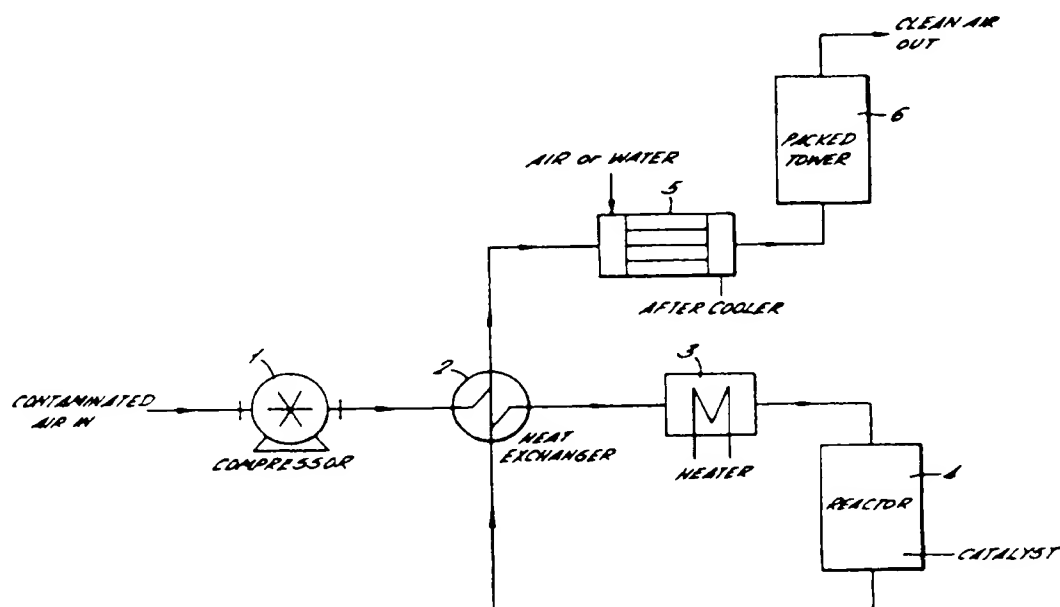
(56) Documents Cited
WPI Abstract Accession No. 81-20161D/12 and
JP560007644 WPI Abstract Accession No.
80-00881C/01 and JP540148187 WPI Abstract
Accession No. 79-46188B/25 and JP540057484

(58) Field of Search
UK CL (Edition N) B1L LAE
INT CL⁶ B01D 53/36 53/70
Online: WPI

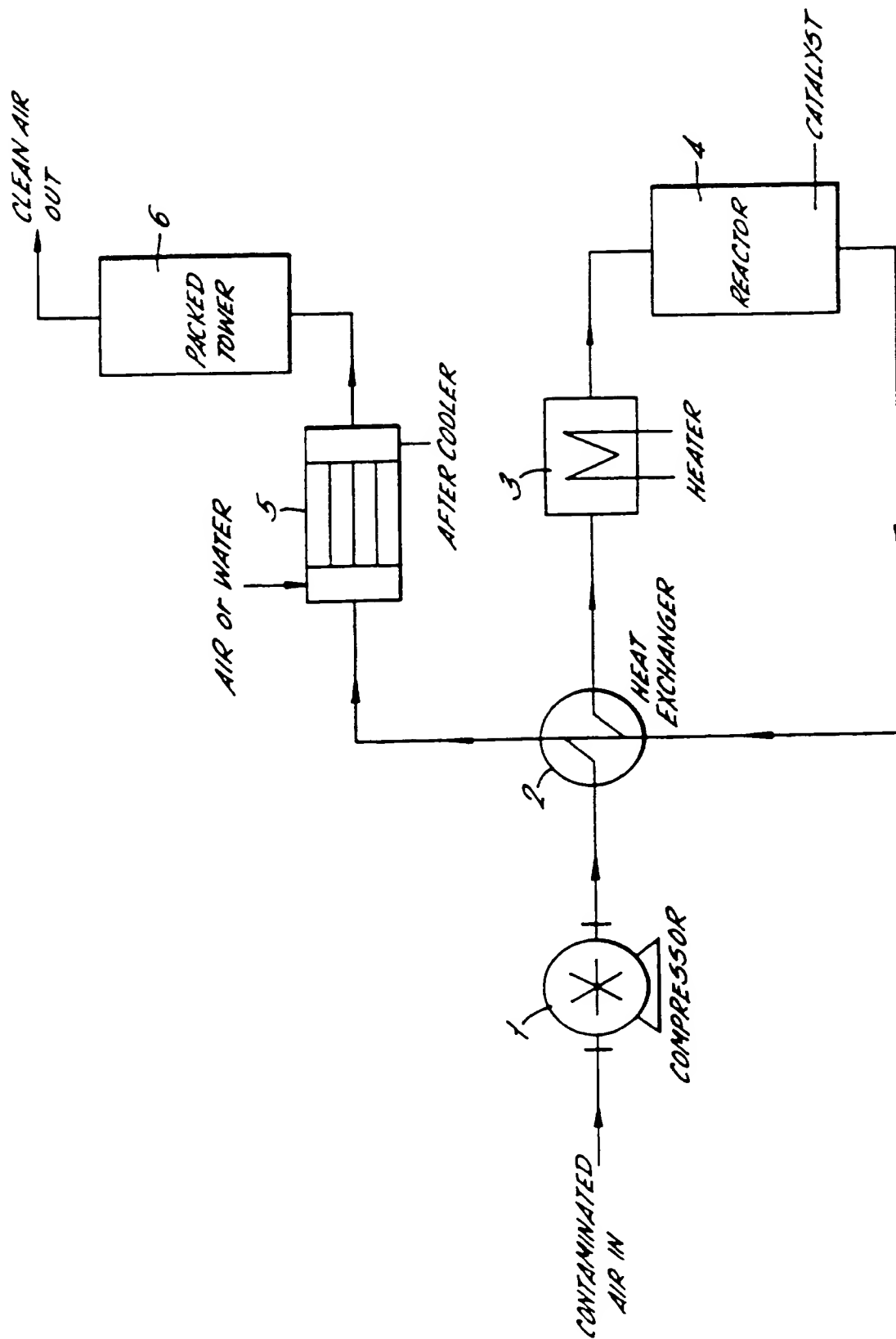
(54) Process for the removal of halogenated organic compounds from air streams

(57) A process for the removal of halogenated organic compounds from an air stream comprising contacting the air stream with a Chi-alumina catalyst.

The process of the present invention may be used to remove halogenated organic compounds such as fluorocarbons, chlorofluorocarbons or chlorocarbons from air streams such as waste gases in which they are contaminants.



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PROCESS FOR THE REMOVAL OF HALOGENATED ORGANIC
COMPOUNDS FROM AIR STREAMS

The present invention relates to a process for the removal of halogenated organic components from air streams. The process involves the use of Chi-alumina as a catalyst.

Many industrial processes produce emissions of volatile organic compounds into air streams which, if not treated, give arise to atmospheric pollution. Operators of such processes are becoming more aware of environmental issues and are increasingly subject to pollution control standards, often via EU directives.

Several methods have been proposed to remove these organic (contaminants) from air streams. For example, organic vapours can be absorbed onto granular or cloth forms of activated carbon with subsequent regeneration of the organic compound using, for example, steam. Alternatively, if the contaminant is water-soluble it may be removed by scrubbing in a packed tower. However, in many instances the above methods are unsuitable because, (a) most organic vapours are insoluble or sparingly soluble in water, (b) many organic vapours such as vinyl chloride monomer, halogenated solvents such as methylene chloride, chloroform, carbon tetrachloride and chlorofluorocarbons are toxic to the extent that acceptable environmental emission standards require that the contaminant in the air stream is removed to a low concentration such that it is not economically viable to adsorb the contaminant on activated carbon or other adsorbents and (c) many organic compounds containing oxygen, for example aldehydes, ketones, esters and oxygen-bridged heterocyclic compounds spontaneously ignite in the presence of air, when adsorbed on activated carbon.

A catalytic purification process for waste gases

containing chlorinated hydrocarbons is described in *Catalysis Today*, 17 (1993), 383-390, Muller *et al* and EP-A-0308789. The process involves a two-bed catalytic system consisting of a doped and stabilized activated Al_2O_3 guard catalyst and a bimetallic Pd,Pt/ Al_2O_3 oxidation catalyst.

The present invention relates to a method for the removal of halogenated organic contaminants from an air stream using catalytic decomposition/oxidation thereby avoiding the difficulties outlined above and which does not involve the use of precious metal catalysts.

Accordingly the present invention provides a process for the removal of halogenated organic compounds from an air stream comprising contacting the air stream with a Chi-alumina catalyst. By the term "removal" is meant the removal of a substantial part of at least the halogenated organic compounds from the air stream. Preferably the air stream is recovered after passage through the catalyst.

Chi-alumina is an activated alumina with a chi-crystal structure which may be formed by controlled heating of aluminium hydroxide in the low temperature range (250° to 800°C) to remove most of the water of constitution. Gibbsite ($\alpha\text{-Al}(\text{OH})_3$) is generally used as the starting material and the production of Chi-alumina from Gibbsite is described by K.P. Goodboy and J.C. Downing, *Activated and Catalytic Aluminas*, pages 93 to 98. The decomposition products from the catalytic breakdown of halogenated organic compounds are normally carbon dioxide and/or carbon monoxide and the halo-acid corresponding to the halogens present.

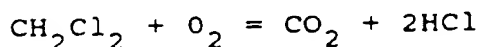
Water and/or oxygen may also be involved either as a reactant or a product in any decomposition reaction. Occasionally, other products may be formed

by rearrangement or partial oxidation. However, this usually only occurs if the system is not running at the optimum condition for complete breakdown for the given halogenated organic compound.

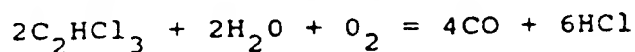
Halogenated organic compounds which may be treated according to the process of the present invention include dichloromethane, trichloroethylene, ethylene dichloride, dichlorofluoromethane, 1,1,2,2-dichlorotetrafluoroethane, dichloroethane, other chlorofluorocarbons, fluorocarbons and chlorocarbons.

Some equations for typical breakdown reactions according to the present invention are as follows:-

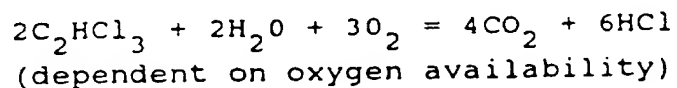
dichloromethane breakdown,



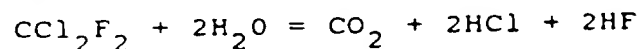
trichloroethylene breakdown,



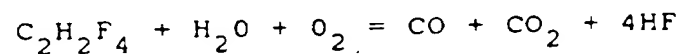
or



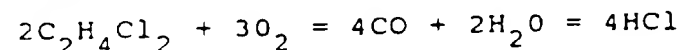
CFC 12 breakdown



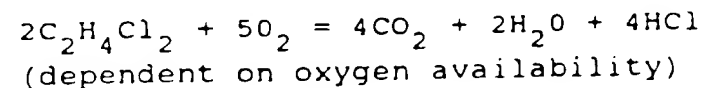
HFC 134a breakdown,



ethylene dichloride breakdown,



or



Preferably, the contaminated air stream is heated prior to contact with the Chi-alumina catalyst. The air stream is preferably heated to a temperature of up to 600°C, the optimum results of the process are obtained when the air stream is heated to a temperature in the range of from 300°C to 500°C before contact with the Chi-alumina catalyst. Contact with the Chi-alumina catalyst may be effected by passage of the air stream through the catalyst or over the catalyst or by any other means.

Preferably the process also includes a step or steps of recovering the treated air stream and removing any decomposition/oxidation product from the recovered air stream. This results in a purified recovered air stream which can be safely discharged into the atmosphere.

In all cases, decomposition products include an acid which can be removed from the exhaust stream by an alkaline medium, e.g. by soda lime or caustic liquid scrubbing. Any carbon monoxide produced can be catalytically oxidised to carbon dioxide, provided that excess oxygen is present. Whether either or both of these processes are needed will depend on the application and on discharge consent levels.

Preferably the air stream recovered from the catalytic process is cooled before passing through an alkaline medium. The exhaust stream is preferably cooled to temperature of 50°C or below, more preferably in the range of from 20°C to 40°C.

It is preferable to reduce the temperature of the exhaust air stream prior to absorbing the acid gases on a solid absorbent, such as soda lime. At temperatures greater than 50°C, the capacity of soda lime for acid gases is significantly reduced. Similarly, air stream temperatures of less than 50°C are desirable in a liquid scrubbing system so

The preferred space velocity of the contaminated air stream (gas flowrate at normal temperature and pressure divided by catalyst volume) is in the range 3000 h⁻¹ to 5000 h⁻¹. Chi-alumina has been found to promote effectively the decomposition/oxidation of halogenated hydrocarbons and it is compatible with the acid decomposition product over long periods.

A preferred embodiment of the present invention will now be described by way of example only with reference to the accompanying drawing, Fig. 1, which shows a flow diagram for the process according to the invention.

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packed bed reactor (4) of the Chi-alumina catalyst where the organic vapour is decomposed or oxidised. The air stream leaves the reactor, passes through the back-to back heat exchanger (2) where it is partially cooled by heat exchange with the in-coming air stream and then passes through an after-cooler (5) which may be air-cooled or water-cooled. The cooled air stream is then passed through an alkaline medium such as a tower packed (6) with soda lime or caustic solution where the acid gases resulting from the decomposition/oxidation of the organic molecule are removed. The air stream depleted of the acid gases can then be safely discharged to the atmosphere.

Preferred embodiments of the present invention will now be described in detail in the following examples:

Example 1

Air contaminated with dichlorodifluoromethane at a concentration in the range of 250 vpm to 2000 vpm and at a flowrate of about 30 m³/hr and at normal ambient temperature and pressure was passed through an apparatus as described in Fig. 1. The catalyst bed volume was 0.007 m³ and the air stream was increased to a temperature of 410°C \pm 5°C prior to its entering the catalyst bed.

The air stream was cooled to a temperature of 40°C after passing through the after-cooler and then passed upwards through a packed bed containing soda lime. Under these conditions and over a continuous operating time of 500 hours the outlet air stream contained a concentration of 2% or less of the dichlorodifluoromethane concentration in the inlet air stream. Acid gas emission from the treated air stream

was maintained at an undetectable level by changing the soda lime canisters at appropriate times. 1 Kg of soda lime completely removed the acid gas products (HCl and HF) from 106 m³ of air containing 500 vpm of dichlorodifluoromethane.

Example 2

In an experiment with the same parameters as used in Example 1, the required temperature to remove 1,1,2,2-dichlorotetrafluoroethane to the same degree was found to be 540°C ± 5°C. With temperatures in excess of 800°C, only about 10% removal of these compounds is possible in the absence of the catalyst.

Example 3

In an experiment with the same parameters as Example 1, 1000 to 2000 vpm of trichloroethylene was removed to the same degree as that in the above examples at a temperature of 350°C ± 10°C.

CLAIMS:

1. A process for the removal of halogenated organic compounds from an air stream comprising contacting the air stream with a Chi-alumina catalyst.
2. A process as claimed in claim 1 further comprising recovering the air stream after contact with the Chi-alumina catalyst.
3. A process as claimed in claim 2 further comprising the step of removing any decomposition/oxidation product from the recovered air stream.
4. A process as claimed in any one of the preceding claims wherein the halogenated organic compound is a chlorofluorocarbon, a fluorocarbon, chlorocarbon or a mixture thereof.
5. A process as claimed in any one of the preceding claims wherein the halogenated compound is dichloromethane, trichloroethylene, ethylene dichloride, dichlorofluoromethane, 1,1,2,2-dichlorotetrafluoroethane, dichloroethane, or a mixture thereof.
6. A process as claimed in any one of the preceding claims wherein the air stream is heated prior to passage through the Chi-alumina catalyst.
7. A process as claimed in claim 6 wherein the air stream is heated to a temperature of up to 600°C.
8. A process as claimed in claim 6 wherein the air stream is heated to a temperature in the range of from 300°C to 500°C.

9. A process as claimed in any one of claims 2 to 8 wherein the recovered air stream is cooled.

10. A process as claimed in claim 9 wherein the recovered air stream is cooled to a temperature of 50°C or below.

11. A process as claimed in claim 9 wherein the recovered air stream is cooled to a temperature in the range of from 20°C to 40°C.

12. A process as claimed in any one of claims 2 to 11 wherein the recovered air stream is passed through an alkaline medium.

13. A process as claimed in claim 12 wherein the alkaline medium is soda lime or a caustic solution.

14. A process as claimed in any one of the preceding claims wherein the Chi-alumina catalyst has a surface area in the range of from 200 to 350m²/g.

15. A process as claimed in any one of the preceding claims wherein the Chi-alumina catalyst has a particle size in the range of from 2mm to 5mm.

16. A process as claimed in any one of the preceding claims wherein the space velocity of the air stream which contacts the catalyst is in the range of from 3000 h⁻¹ to 5000 h⁻¹.

17. The use of Chi-alumina as a catalyst in a process for the removal of halogenated organic compounds from an air stream.

18. A process as claimed in claim 1 substantially as

hereinbefore described with reference to and as illustrated in Fig. 1.

19. A process as claimed in claim 1 substantially as hereinbefore described with reference to Example 1, Example 2 or Example 3.

Search Examiner
D S LUCAS

Date of completion of Search
19 JANUARY 1995

Documents considered relevant
following a search in respect of
Claims :-
1 TO 19

Categories of documents

&: Member of the same patent family; corresponding document

Category	Identity of document and relevant passages	Relevant to claim(s)
X	WPI Abstract Accession No 81-20161 D/12 and JP 560007644 (TOYOTA) see Abstract	1 and 17 at least
X	WPI Abstract Accession No 80-00881 C/01 and JP 540148187 (NISSAN) see Abstract	1 and 17 at least
X	WPI Abstract Accession No 79-46188 B/25 and JP 540057484 (SUMITOMO) see Abstract	1 and 17 at least

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